Influence of Cellulose Ether Particle Size on Water Retention of Freshly-Mixed Mortars

Laetitia Patural, Alexandre Govin, Bertrand Ruot, Olivier Deves, Philippe Grosseau

Communication : 9th CANMET [Canada Centre for Mineral and Energy Technology] /ACI [American Concrete Institute] (International Conference on Superplasticizers and other Chemical Admixtures in Concrete), Séville, 13 au 16 octobre 2009

Influence of Cellulose Ether Particle Size on Water Retention of Freshly-Mixed Mortars

PATURAL, L.[1, 2] **; GOVIN, A.** [1, 2] **; RUOT, B.**[3] **; DEVES, O.** [4] **; GROSSEAU, P.** [1,2]

(1) Département PMCC, Centre SPIN, Ecole Nationale Supérieure des Mines de Saint-Etienne, 158 Cours Fauriel 42023 Saint-Etienne, Cedex 02, France
(2) LPMG UMR 5148, 158 Cours Fauriel, 42023 Saint-Etienne, Cedex 02, France
(3) Centre Scientifique et Technique du Bâtiment (CSTB), Département Enveloppe et Revêtements / Division Caractérisation Physique des Matériaux, 24 Rue Joseph Fourier, 38400 Saint-Martin-d'Hères, France
(4) Centre Scientifique et Technique du Bâtiment (CSTB), Département Enveloppe et Revêtement / Division Enduits, Mortiers et Colles, 84 Avenue Jean Jaurès - Champs-sur-Marne, 77447 Marne-la-Vallée Cedex 2, France

"Paper presented at the 9th CANMET [Canada Centre for Mineral and Energy Technology] /ACI [American Concrete Institute] (International Conference on Superplasticizers and other Chemical Admixtures in Concrete), Séville, 13 au 16 octobre 2009 as an oral communication"

Abstract

Cellulose ethers are polymers frequently introduced into mortar formulations in order to improve water retention capacity and workability of the freshly-mixed materials. Physico-chemical parameters of these admixtures (molecular weight, granulometry, substitution degrees, etc) seem to have a strong influence on mortar water retention capacity. In this paper, the influence of cellulose ether particle size was studied. Two behaviors were highlighted regarding the particle size effect on mortar water retention. On the one hand, for cellulose ethers providing intermediate water retention, this parameter is fundamental: the thinner the particles, the better the water retention. The increase in water retention was explained by the rate of dissolution of every fraction which was faster for the thinnest particles. On the other hand, for admixtures providing strong water retention, the effect of this parameter was weaker or not relevant. Indeed, a cellulose ether concentration threshold was noticed, justifying this behavior.

Keywords:

cellulose ethers ; cement ; mortar ; particle size ; water retention.

I Introduction:

Factory-made mortars are mainly composed of mineral binders (cement, lime and/or gypsum), aggregates and additives (*e.g.* fillers). They also contain different kinds of admixtures, mostly organics (such as latexes and polysaccharides), in order to impart some specific properties to the mortar, from the fresh paste to the hardened material [1]. Among all the polysaccharides, cellulose ethers seem to be the most suitable molecules to produce mortars with adequate water retention ability (*i.e.* higher than 94% up to 99%).

Mortar consistency may contribute to its water retention capacity, but this hypothesis should be checked by further investigations. Indeed, cellulose ethers can induce excellent water retention thanks to the possible superposition of two phenomena [2]:

(i) a rheological effect similar to the one produced by other polysaccharides;
(ii) an effect that could be specific to cellulose ethers, which remains to be defined.

Possibilities include modification of the porous network in the fresh state, osmotic pressure, or the presence of a cellulose ether film acting as a diffusion barrier [3].

Using well-know molecules, it should be possible to understand the function of three types of cellulose ethers on mortar water retention. Particle size and morphology of cellulose ether powders are two parameters which are expected to influence mortar water retention. Here, the influence of cellulose ether particle size on water retention has been studied to understand if both parameters are linked.

II Materials and Methods:

II 1 Mineral Products

Mortars were prepared with "CEReM formulation". A dry mixture was prepared with 30% cement, 65% sand and 5% filler. Grey Portland cement CEM I 52.5 R was employed according to EN 197-1 [4]. Chemical analysis was performed by X-ray fluorescence spectroscopy (XRF). Then, phase compositions (Table 1) were calculated using Bogue formula with CaO correction [5]. Each experiment was performed three times with the results averaged. Sand was siliceous and conformed to standard NF EN 13139 [6]. The filler was calcium carbonate ($CaCO_3$). The organic admixture amount (0.27%) was based on the total dry mixture (*i.e.* cement, sand and filler). The W/C was 1. Mixing procedure was in accordance with EN 196-1 [7].

II 2 Organic admixtures: cellulose ethers

Admixtures are especially prepared products, added in small amounts to mortar during the mixing process in order to improve the properties of the fresh material.

Cellulose, the most abundant polymer in nature, forms a part of the polysaccharide family and is derived from β-D-glucopyranose. Cellulose ethers are obtained by alkalization or alkylation of cellulose. In this paper, three kinds of cellulose ethers were studied: hydroxypropylmethyl cellulose, noted as HPMC (Figure 1a), hydroxyethylmethyl cellulose, noted as HEMC (Figure 1b) and hydroxyethyl cellulose, noted as HEC (Figure 1c).

On Figures 1a, 1b, and 1c, substituent positions are arbitrary; they differ from one molecule to another. Ten cellulose ethers were selected to study particle size influence on water retention: 4 HEC, 3 HEMC and 3 HPMC (Table 2). It is interesting to note that these cellulose derivatives are widely used in many industrial fields of application such as cosmetics, pharmaceuticals, paints, textiles and mineral industries. In our studied field, cellulose products are used as water-retaining agents, thickeners, binders, and film formers.

The number of substituted hydroxyl groups (OH) per anhydroglucose unit is expressed as *DS* (Degree of Substitution). Moreover, the molar ratio of alkoxy groups (hydroxypropyl, hydroxyethyl, and methoxyl) in the side chains to cellulose is expressed as the average Molecular Substitution (*MS*).

All polysaccharides were characterized by Size Exclusion Chromatography (SEC) in order to determine their average molecular weights [8]. This chromatographic method separates molecules relating to their size. SEC analysis was performed on a Waters apparatus equipped with a pump (Waters 916) and a refractometer-type detector (Waters 2410). The specific column used for polysaccharide SEC was a Tosohaas TSK Gel GMPWXL column. The eluent was a 0.5 $mol.L^{-1}$ sodium chloride solution in order to avoid agglomeration. It was filtered and on line-degassed. The flow rate was set to 0.5 $mL.min^{-1}$. The column was kept at 35°C in an oven.

II 3 Cellulose ethers particles size separation

To separate cellulose ethers powders, a sieve shaker was used in order to divide the powders into 4 or 5 fractions ranging from 100 to 200 µm.

In addition, the particle size distribution was accomplished using a laser diffraction granulometer (Mastersizer 2000, Malvern), in dry dispersion.

II 4 Cellulose ethers dissolution rate

The rate of dissolution of cellulose ether was monitored, in saturated lime solution, in order to be close to CEReM mortar conditions (high pH value). The admixture quantity was adjusted to obtain a polysaccharide concentration equal to 9 $g.L^{-1}$ (equivalent to CEReM mortar). Experiments were performed in a glass reactor controlling the temperature at 23°C. The stirring system consisted of a turbine with four blades.

The cellulose ether was titrated using a colorimetric method described by Dubois [9]. This method consisted of adding 0.25 mL of 80% phenol solution and 1.3 mL of sulphuric acid to 0.5 mL of supernatant (obtained after 5 minutes centrifugation) in tubes. Then, they were closed and vortex-stirred. After cooling down for 20 minutes, the solution absorbance was measured at 490 nm using a UV/Visible spectrophotometer (CARY 300 Scan, Varian).

II 5 Water retention measurements

Water retention is a mortar property avoiding the rapid loss of water to substrate by suction (and also evaporation, to a lesser extent). This property prevents bleeding or "water loss" when the mortar is in contact with relatively permeable units. Retention is a fundamental property, which affects workability and bonds between mortar and masonry. The water retention capacity will depend on the composition of the mortar.

According to the DTU 26.1 [10], mortars can be divided into three classes. The first one (low water retention category) is for mortars with a water retention lower than 86%. The second class (intermediate) corresponds to values ranging from 86% to 94%. The last one (strong) is defined by water retention higher than 94%, corresponding to the required values. These limits have to be handled with care as they refer to ASTM C91 measurements [11]. In this study, water retention measurements were performed using two different standardized methods: standard DIN 18555-7 [12] and standard ASTM C91. Our results showed that both methods produce similar results (see "Correlation between ASTM C91 and DIN 18 555-7 test methods"). Consequently, only ASTM measurements will be presented in this paper.

ASTM measurements have to be performed 15 minutes after mixing. The aim of the test is to measure the loss of water of a mortar under a 50 mm Hg (6.6x103 Pa) vacuum for 15 minutes (Figure 2). After that, the water retention capacity, noted as WR, is calculated using the following equation:

$$WR\ (\%) = \frac{W_0 - W_1}{W_0}\ x\ 100$$

W_0 represents the initial mass of mixing water, and W_1 is the mass of mixing water lost after 15 minutes after aspiration.

III RESULTS and DISCUSSION

III 1 Correlation between ASTM C91 and DIN 18 555-7 test methods

The comparison between both methods is shown on Figure 3. Usually, both methods produced relatively similar results, except for three HEC samples, which imparted a more fluid property to the mortar. The water retention obtained with the DIN method was close to 90% while the result of ASTM was higher (roughly 97%). This can be explained by a bleeding phenomenon observed for these admixtures during the experiment.

Overall, the ASTM values were generally slightly higher than those obtained with the DIN method. This phenomenon can be explicated by a vacuum effect. Indeed, ASTM measurements were carried out under vacuum (50 mm Hg). On the contrary, the DIN method

evaluated the water absorption of a mortar in contact with a filter paper, based on gravity and capillarity, and performed at atmospheric pressure.

All things considered, the DIN 18555-7 and the ASTM C91 methods are two ways to determine the water retention. Both methods are roughly comparable.

III 2 Cellulose ethers: effects of particle size

First, granulometry results were generally slightly higher than the cut threshold results of the sieve. These differences can be explained by cellulose ether particle shape. As a matter of fact, some of the particles had a fibre like appearance.

HEC — Cellulose ether particle size is generally considered as a fundamental parameter influencing mortar water retention. First, the effect of HEC particle size was investigated. Among the four HEC samples, the main difference was the molecular weight. H1 and N1 had low molecular weights (respectively 45 and 40 kDa), whereas H7 and N4 had higher molecular weights. On the one hand, H1 and N1 particle size had an effect on mortar water retention (Figure 4). Indeed, for H1, water retention capacity ranged from 87% to 94% for particle sizes ranging from 150-200 µm to a diameter lower than 100 µm, respectively. Thus, for low molecular weight HEC, the smaller the particles, the better the water retention. Moreover, N1 and H1 had equivalent molecular weights whereas *MS* decreased from 2.5 to 1.9, respectively. Water retention was equal to 93% for N1, and to 95% for H1. Therefore, for constant molecular weight HEC, water retention was improved when *MS* decreased.

On the other hand, for N4 (1 500 kDa), particle size impact was weaker than with H1 and N1. Actually, for the thinner fraction (diameter lower than 100 µm), water retention was equal to 98%, whereas, for the thicker fraction (diameter higher than 200 µm), water retention capacity was about 96%. In the same way, for H7 (790 kDa), the water retention was similar, and was roughly equal to 99% independent of the particle size. In addition, as for low molecular weight HEC, *MS* seemed to influence water retention. While molecular weight decreased from 1 500 kDa (N4) to 790 kDa (H7), *MS* slightly diminished from 2.5 to 2.4, and water retention was enhanced from 98% to 99%.

To summarize the influence of HEC particle size, for HEC with low molecular weights, the thinner the particles, the better the water retention. On the contrary, for HEC with high molecular weights, the influence was weaker or not relevant. *MS* impact was noticed for both HEC groups. Water retention capacity was improved when *MS* decreased.

HEMC — Among this group, molecular weight increased between C2 to C4. HEMC C7 had a higher molecular weight and a higher *MS* than C2 and C4. First, for HEMC C2 (Figure 5), mortar water retention varied for every particle size fractions. No real trend was evident. Fractions #3 (125-150 µm) and #1 (<100 µm) had the lowest water retention values (about 93%). Two others fractions, #4 (150-200 µm) and #2 (100-125 µm), provided higher water retention capacities. These variations may be explained by difference in morphology, or molecular weight. For HEMC C4, mortar water retention was roughly constant and independent of the particle size. Finally for C7, despite a rise in molecular weight, water retention was lower than C4. This can be elucidated by an increase in *MS* from 0.15 to 0.29 from C4 to C7. Moreover, a small influence of the particle size was noticed for C7.

HPMC — HPMC group consisted of three polymers with the same degrees of substitution (DS = 1.75 and MS = 0.1), while molecular weight went up from J1 to J3.
J1 particle size influenced water retention capacity (Figure 6). As a matter of fact, water retention increased as particle size decreased. However, for J2, this influence was weaker. Water retention ranged from 98% to 99% as particle size ranged from 150-200 µm to less than 100 µm. Finally, J3 did not influence mortar water retention.

In conclusion, two different behaviors were highlighted. On the one hand, for cellulose ethers with low molecular weights, the particle size influenced water retention. On the other hand, for admixtures with higher molecular weights, the influence of the particle size was smaller or not significant.

To elucidate these two behaviors, two hypotheses can be proposed. For the first comportment, particle size influence can be interpreted by differences in the rate of dissolution for each particle size fraction. For the second class, it can be interpreted by the presence of a cellulose ether concentration threshold value. From this threshold, mortar water retention would be still constant and independent of the cellulose ether concentration.

III 3 Cellulose ether dissolution rate

As observed for HEC H1, the thinner the particles, the better the water retention. The rate of dissolution of every particle size fractions was studied for this admixture.

Dissolution rate was monitored for the thinnest (< 100 µm) and the thickest fraction (150-200 µm) of H1 (Figure 7). As expected, the thinnest fraction dissolved faster than the thickest fraction. Indeed, to dissolve 90% of the total cellulose ether quantity, 11 minutes were necessary for the fraction lower than 100 µm, whereas 24 minutes were required for the fraction ranging from 150 to 200 µm.

In conclusion, a particle size diminution led to an augmentation of the rate of dissolution of these particles and, consequently, in mortar water retention. For the thinnest particles, the water retention values were higher because the suitable soluble cellulose ether quantity was reached in less time. On the contrary, for thicker particles, when water retention measurements were performed, the particles were not totally dissolved. Hence, the water retention was lower because the suitable polymer quantity was not dissolved. Although the experiment will not comply with the standard DIN 18555-7, the delay between mixing and retention measurement may be extended to achieve optimal water retention.

III 4 Influence of cellulose ether concentration

When particle size has no effect on mortar water retention, there may exist a threshold value in admixture concentration above which water retention remains constant. To check this hypothesis, the water retention was studied as a function of the cellulose ether concentration. In Figure 8, the water retentions of two HEC samples are shown. First, when H1 concentration rose from 3.3 g/L to 13.3 g/L, the water retention was improved from 80% to 98%. However, for HEC H7, the evolution is weaker.

Besides, the water retention corresponding to 9 $g.L^{-1}$ of cellulose ether (CEReM mortar conditions) seemed to be reached at a lower concentration (roughly [H7] ≈ 5-7 $g.L^{-1}$). Consequently, whatever the particle size, if the solution contained an adequate amount of solubilised polymer, the water retention would not change.

IV Conclusion

The addition of cellulose ether improved mortar water retention. This property was influenced by polymer particle size depending on admixture molecular weight. Indeed, for low molecular weight cellulose ethers (providing an intermediate water retention), the thinner the particles, the stronger the water retention capacity. This behavior was explained by differences in the rate of dissolution of each fraction. On the contrary, for high molecular weight cellulose ethers (providing a strong water retention), the impact of particle size was very small or not significant. As a matter of fact, water retention was not affected by this parameter because the suitable polymer quantity could be reached independently of the particle size fraction. However, for high molecular weight polymer, the water retention was strong. Hence, the influence of particle size may not be observed because water retention

values could be too high. The cellulose ethers used in this study may not sufficiently discriminate water retention differences.

Acknowledgment

The author would like to acknowledge all the industrial and academic CEReM members for their financial and technical support (http://cerem.cstb.fr).

References

[1] Ruot B., Goto T. and Pourchez J., "Some aspects of cellulose ethers and latexes influence on the properties of cement-based materials - Examples of results obtained within the CEReM", Proceedings of the VII SBTA (7° Symposio Brasileiro de Tecnologia das Argamassas), Recife, Brazil, 1-4 May 2007.

[2] Pourchez J., Aspects physico-chimiques de l'interaction des éthers de cellulose avec la matrice cimentaire, PhD thesis, École Nationale Supérieure des Mines de Saint-Étienne, November 2006, 285 p.

[3] Jenni A., Holzer L., Zurbriggen R. and Herwegh M., "Influence of polymers on microstructure and adhesive strength of cementitious tile adhesive mortars," Cement and Concrete Research, vol. 35, 2005, pp. 35-50

[4] EN 197-1, Cement. Part 1: Composition, specification and conformity criteria for common cements, February 2001.

[5] Taylor H.F.W., Cement Chemistry, The chemistry of Portland cement manufacture, Telforf, 1997.

[6] NF EN 13139, Granulats pour mortiers - Spécifications des caractéristiques des granulats et fillers utilisés dans les mortiers, January 2003

[7] EN 196-1, Methods of testing cement - Part 1: Determination of strength, April 2006.

[8] Clasen C. and Kulicke W.M., "Determination of viscoelastic and rheo-optical material functions of water-soluble cellulose derivatives", Progress in Polymer Science, vol. 26, 2001, pp. 1839-1919.

[9] Dubois M., Gilles K.A., Hamilton J.K., Rebers P.A. and Smith F., "Colorimetric method for determination of sugars and related substances". Analytical chemistry, vol.28, n°3, 1956, pp. 350-356.

[10] NF DTU 26.1 P1-2, Travaux d'enduits de mortiers - Partie 1-2: Critères généraux de choix des matériaux, April 2008.

[11] Standard C91 section 7.2 and 7.3 - Specification for masonry cement: determination of water retention and air content, American Society for Testing Materials, 2003.

[12] Standard DIN 18555-7: Testing of mortars containing mineral binders; part7: Determination of water retentivity of freshly mixed mortar by the filter plate method, Deutsches Institut für Normung, 2000.

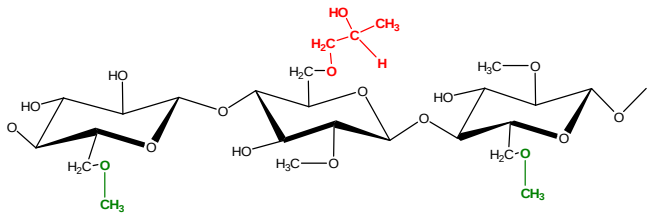
Table 1: Chemical and phase composition of the investigated cement.

Chemical composition (% wt)				Phase composition (% wt)	
Oxides	XRF	Oxides	XRF	Phases	XRF (Bogue)
CaO	66.3 ± 0.2	MgO	0.99 ± 0.01	C_3S	64.3 ± 0.8
SiO_2	22.3 ± 0.1	P_2O_5	0.24 ± 0.01	C_2S	15.5 ± 0.3
Al_2O_3	3.40 ± 0.01	TiO_2	0.18 ± 0.18	C_3A	4.2 ± 0.1
SO_3	3.04 ± 0.03	K_2O	0.04 ± 0.04	C_4AF	8.7 ± 0.1
Fe_2O_3	2.87 ± 0.03	MnO	0.016 ± 0.001	Sulphates	3.04 ± 0.03

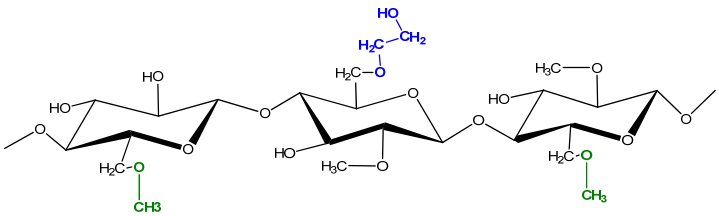
Table 2: Cellulose ethers (HEC – HEMC – HPMC) used in this work.

HEMC	$\overline{M_w}$ (kDa)	Hydroxyethyl group (% OC_2H_4OH)	*MS*	Methoxyl group (% OCH_3)	DS
C2	180	4.8	0.15	27.4	1.7
C4	380	4.8	0.15	27.4	1.7
C7	660	9.0	0.29	23.8	1.5
HPMC	$\overline{M_w}$ (kDa)	Hydroxypropyl group (% OC_3H_6OH)	*MS*	Methoxyl group (% OCH_3)	DS
J1	225	2.98	0.1	28.2	1.75
J2	630	2.98	0.1	28.2	1.75
J3	910	2.98	0.1	28.2	1.75
HEC	$\overline{M_w}$ (kDa)	Hydroxyethyl group (% OC_2H_4OH)	*MS*		
H1	45	45.3	1.9		
N1	40	56.0	2.5		
H7	790	52.5	2.4		
N4	1 500	56.0	2.5		

(a)



(b)



(c)

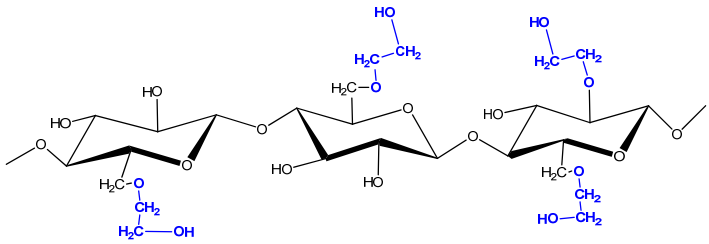


Figure 1: Molecular structure of cellulose ethers ((a) HPMC, (b) HEMC, (c) HEC).

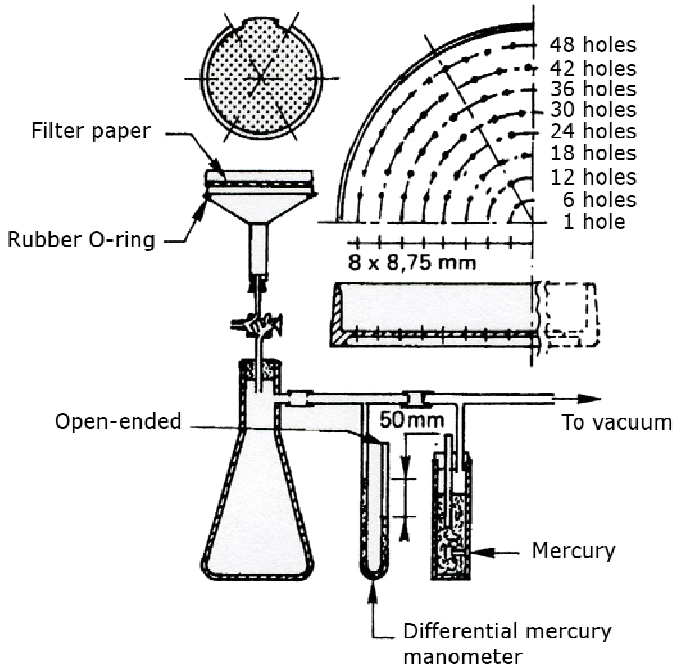


Figure 2: Experimental device to measure water retention with standard ASTM C91.

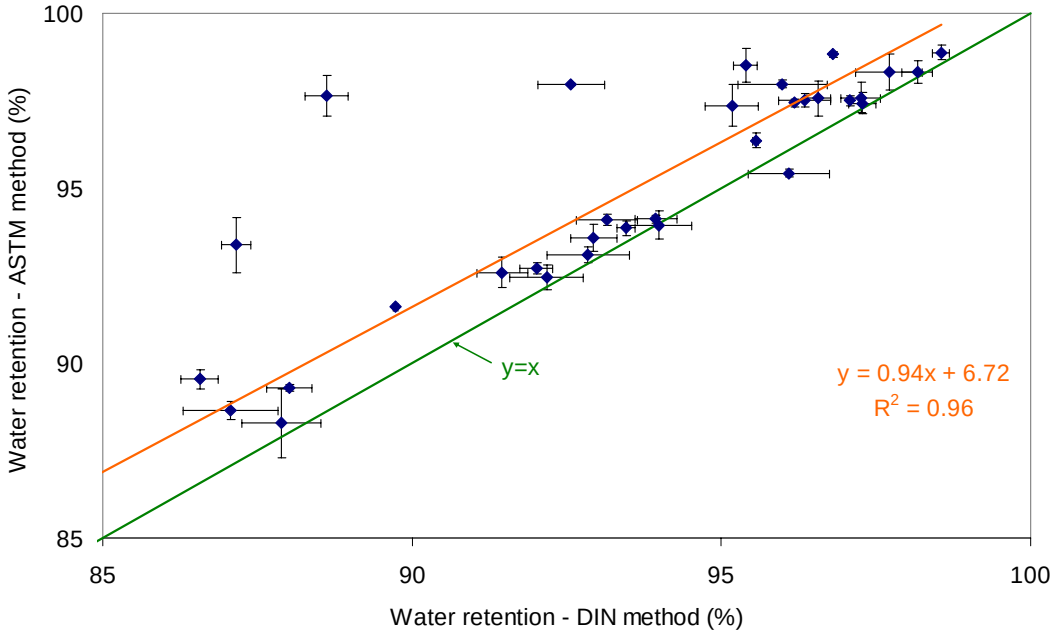


Figure 3: Comparison between the DIN and the ASTM method.

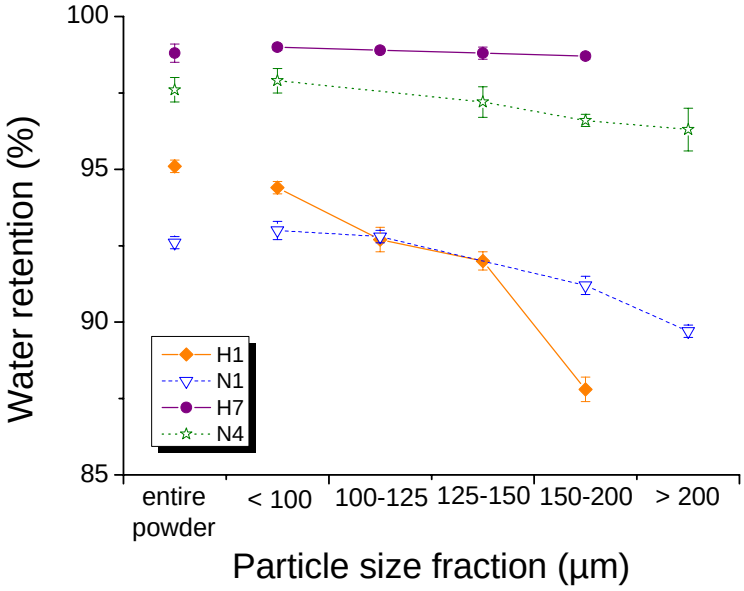


Figure 4: Influence of HEC particle size on water retention.

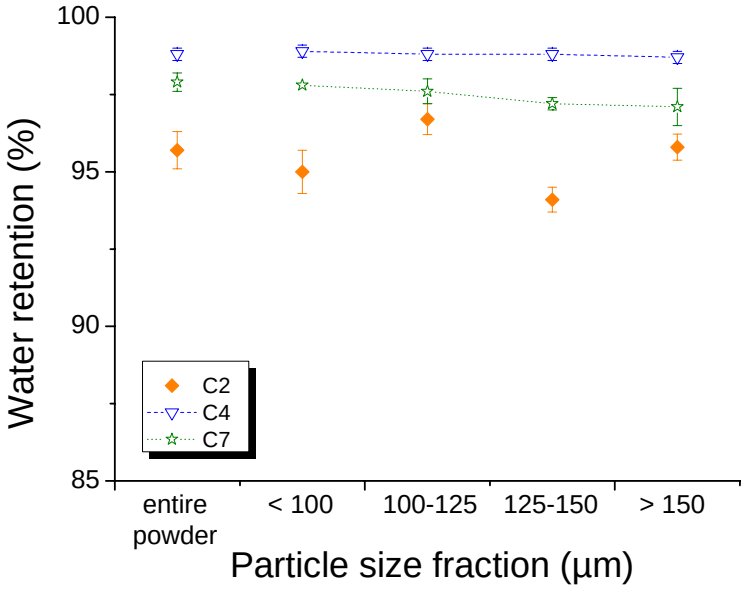


Figure 5: Influence of HEMC particle size on water retention.

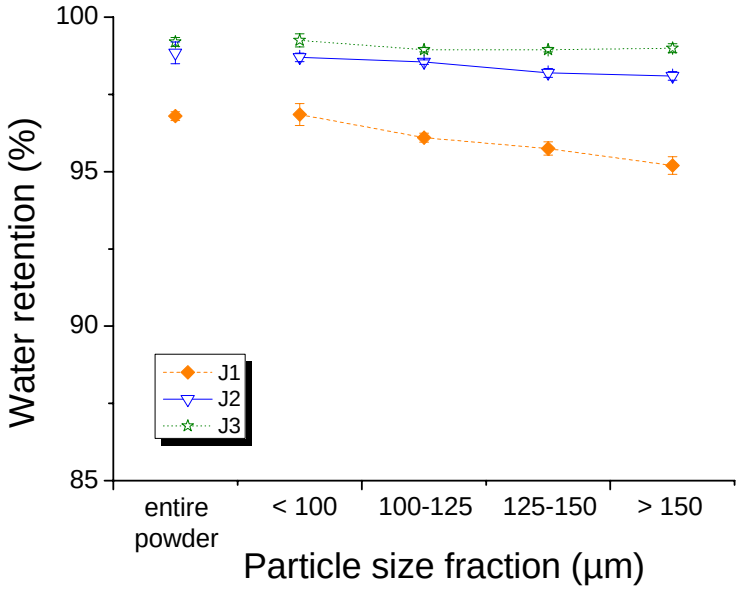


Figure 6: Influence of HPMC particle size on water retention.

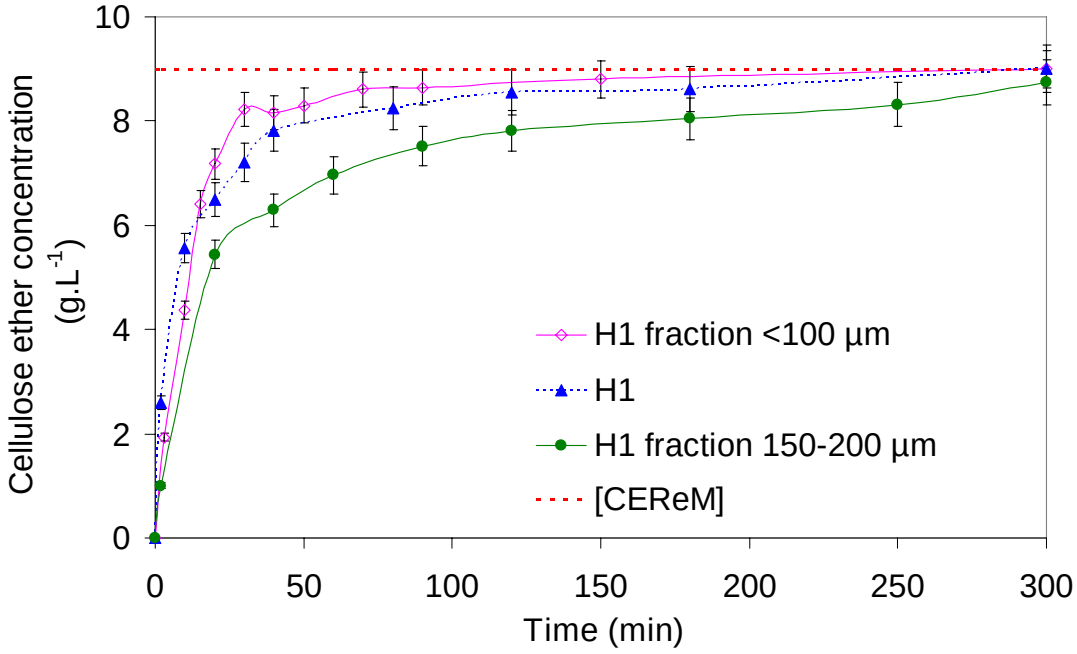


Figure 7: Dissolution rate of H1 and its particle size fractions.

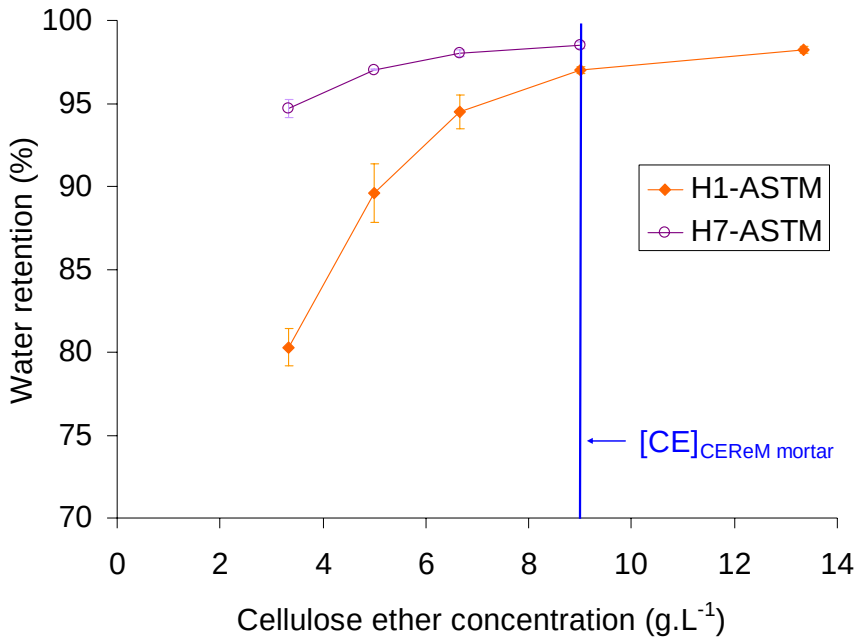


Figure 8: Influence of HEC concentration on water retention.